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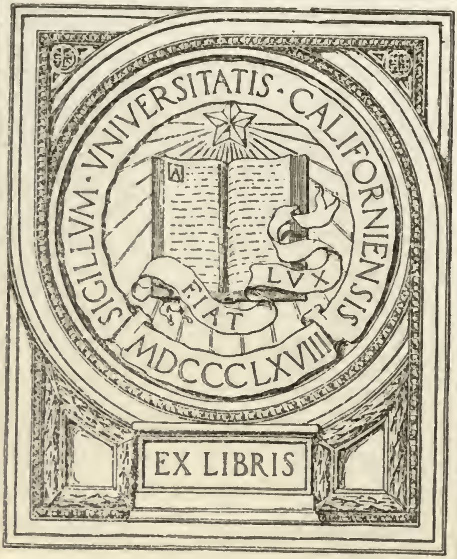

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The Effect of Substitution on the Free Energy of Reduction of Benzoquinone.

Including

A STUDY OF THE ELECTROMETRIC TITRATION METHOD OF MEASURING POTENTIALS

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE IN
COLUMBIA UNIVERSITY

BY

LILLIAN ELOISE BAKER, M.A.

NEW YORK CITY

August 5, 1922

The Jackson Press, Kingston
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Dedicated to

MISS CHARLOTTE BRAGG

Wellesley College

EXCHANGE

ACKNOWLEDGMENT

The author wishes to express her sincere thanks and appreciation to Dr. Victor K. La Mer for suggesting the method of attack and for advice in carrying out the work.

OUTLINE OF THESIS

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ABSTRACT OF DISSERTATION

1. What was attempted?

2. In how far were the results successful?

3. What contribution actually new to the science of chemistry has been made?

1. The primary object of this work was to study quantitatively the effect of substituent groups on the free energy of reduction of the quinone nucleus by means of potential measurements.

2. The work has been successful in that

    a. It has established the validity of the titration method beyond question.

    b. Technique and apparatus have been developed so that it is possible to obtain a precision of ±0.3 mv. over a wide range of concentrations, and an average deviation of only 0.2 mv.

    c. A beginning has been made on the study of the relation of the structure of organic compounds to the free energy of reduction comprising a study of twelve compounds.

3. A quantitative measurement has been made of the influence of eight important groups on the free energy of reduction when substituted in the benzoquinone nucleus, thus obtaining information that will be valuable in the synthesis of oxidation reduction indicators, in interpreting the reactions of compounds, and posably also in determining their structure.

INTRODUCTION

Purpose of the Work

Although it has been shown[1, 2] that the oxidation and reduction of at least certain organic compounds can be explained according to the theories established for inorganic chemistry from which it should be possible to choose an oxidizing or reducing agent as well as the conditions of acidity and concentration necessary for a particular reaction from a consideration of the energy relations involved, nevertheless it is still necessary to make such selections in a more or less empirical manner because so little quantitative data is available that reasoning from general principles is impossible. It is, therefore, highly important to obtain data on the normal potentials of organic compounds and to determine the quantitative influence that substituent groups exert in different types of nuclei. The meagreness of such data is due largely to the labor required in determining concentrations and the time necessary to reach equilibrium when the potentials are measured by the customary method of pure mixtures. Also considerable doubt has been felt concerning the validity of methods using secondary oxidizing materials of an inorganic nature to shorten this time. It has accordingly been the purpose of the present investigation to test the validity and precision of the more rapid electrometric titration method as a means of measuring potentials and then to utilize this method in a systematic study of the effect of substitution on the free energy change of oxidation-reduction reactions. This paper is, therefore, the beginning of work determining the relation of structure of organic compounds to their oxidation-reduction potentials and the free energy change involved.

Selection of a Nucleus

The system chosen for this work (benzoquinone and its derivatives) was selected because:

1. It has been shown that the quinone-hydroquinone system conforms to the Vant Hoff isotherm. It is strictly reversible and comparatively free from side reactions that would introduce difficulties.

[1] Haber and Russ, Z. Phys. Chem. *47*, 294 (1904).
[2] Granger and Nelson, Jour. Am. Chem. Soc. *43*, 1401 (1921).
Granger, Dissertation, Columbia University (1920).

2. Two investigators[3, 4] have already determined the reduction potential of quinone-hydroquinone by the method of pure mixtures, thus giving data valuable for the comparison of the two methods.

3. The quinoid structure occupies an important place in the theory of organic dyestuffs.

4. The synthesis of a series of dyes to act as oxidation reduction indicators for use in biological work, similar to the series of hydrogen ion indicators has been suggested by Clark.[5]

5. It may furnish data for the improvement of the quinhydrone electrode as an alternative to the hydrogen electrode in electrometric acidity titration as suggested by Dr. La Mer.

6. Some previous work[6, 7] has indicated that data upon oxidation-reduction potentials of hydroquinone derivatives may throw considerable light on the nature of the structure and destruction of the antiscorbutic vitamin.

Historical

The measurement of the available energy of a chemical reaction has long attracted the attention of chemists as one of the greatest import, for from such information much can be predicted concerning the reaction. The problem involves a concept of an affinity or attractive force between the molecules of matter.. At first, scientists attempted to measure this force by the speed of the reaction and by the heat developed during the process, but a study of the thermodynamics of reversible reactions has shown the unreliability of these methods. Von Helmholtz was the first to demonstrate conclusively that the only true measure of the chemical affinity between substances that manifests itself by a chemical reaction is the decrease in the free energy of the system or the maximum amount of available work that a reaction can produce when conducted reversibly at constant volume and temperature in passing from its initial state to that of equilibrium.[8] This principle

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[3] Granger and Nelson, ref. 2.

[4] Sorenson, Compt. Rend. Lab. Carlsberg, Vol. 14, No. 14 (1921).

[5] Clark, M., Jour. Wash. Acad. Sci. *10*, 255 (1920).

[6] Bezssonoff, Compt. Rend. *173*, 466 (1921).

[7] La Mer, Dissertation, Columbia University (1921).
Jour. Ind. Eng. Chem. *13*, 1108.

[8] In this paper the term free energy is used as defined by Lewis, i.e. the maximum work at constant temperature and pressure. Jour. Am. Chem. Soc. *35*, 14 (1913).

was later rediscovered and emphasized by Vant Hoff and is expressed concisely in the Vant Hoff isotherm,

$$W=RT \log K - RT \log \frac{C_3 \times C_4}{C_1 \times C_2}$$

There are four methods available for the measurement of maximum work or free energy change:

1. Calculation of the equilibrium constant of a reaction from analytical data.

2. Measurement of the vapor pressure or osmotic pressure at equilibrium.

3. Electromotive force measurements.

4. Indirect calculation from the Nernst heat theorem.

The first method is inapplicable in most cases as the reaction proceeds so far in reaching equilibrium that the concentrations of some components are too minute to admit of determination by analytical methods. The second method is obviously impossible of general application due to the difficulty of measuring minute osmotic or vapor pressures. The E.M.F. method has been quite generally and extensively used in the field of inorganic chemistry and its validity confirmed by Knupffer and Bredig.[9] Recently Dr. Granger[10], working under the direction of Professor Nelson of this laboratory, investigated the system quinone-hydroquinone by studying the potentials of mixtures of differing concentrations at different acidities and showed conclusively that the Vant Hoff isotherm (or Peters' equation for the E.M.F. developed) applied to reversible organic as well as inorganic reactions, obtaining results in quite as close agreement with it as those of most inorganic systems. However, in using this method of pure mixtures, Granger[10] found it necessary in order to measure the concentrations of the components, to use solutions saturated with either quinone and quinhydrone, or hydroquinone and quinhydrone, calculating their concentrations from solubility determinations and the determination of the dissociation constant of quinhydrone. This in itself is too stupendous a piece of work to apply to many systems. Also it was found that no true equilibrium was reached. The potentials as a rule rose for the first few hours and then fell con-

[9] Z. Phys. Chem. *26*, 255 (1895).
[10] Granger and Nelson, ref. 2.

tinuously, though slowly, for 336 hours or as long as the experiment was continued. It was necessary to determine the potentials by extrapolation to zero time or by taking the values most nearly constant, a device which introduces a factor of uncertainty. Moreover, in the time required by the method of pure mixtures appreciable chlorination from the hydrochloric acid in which the quinone and hydroquinone were dissolved often occurred.

That the time required for the attainment of equilibrium may often be greatly shortened by the addition of a secondary substance such as KI as a catalyzer or potential intermediate ("Vermittler") was shown by Haber and Russ[11] for the quinone-hydroquinone system and by Loimaranta and Abegg[12] for the arsenite-arsenate system. Luther[13], however, questioned the reliability of all methods that employ extraneous materials lest the potentials so measured be those of the added substance and not those of the specific components desired, and outlined the criteria that must be met in order that potentials measured with inert electrodes such as gold or platinum may be considered to be those for the specific oxidation reduction system under examination. These methods were, therefore, apparently abandoned until 1920 when Clark[14] introduced the method of using the secondary material (in this case titanous chloride) as a titrating agent and thereby gave a means of altering the concentration of the components and of calculating directly the concentrations of the oxidized and reduced forms from the volume of the titrating agent used and the volume required for complete reduction. Clark infers that his potentials are the correct ones since he obtains nearly constant values for different concentrations, but offers no other proof of the validity of his method of measurement. It will be shown from the data which follow that the potentials measured by the titration method meet all the criteria proposed by Luther and in addition satisfy the still more rigorous test of approaching the equilibrium from either side.

This investigation is the first to have as its object the systematic study of the quantitative effect of substituent groups on the free energy of reduction. During the preparation of this paper Conant[15] *et al.* have published some data giving the effect of one group

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[11] Haber and Russ, ref. 1.
[12] Loimaranta and Abegg, Z. Electrochem *13*, 34 (1907).
[13] Luther, ibid. *13*, 289 (1907).
[14] Clark, ref. 5.
[15] Conant, Kahn, Fieser, and Kurtz, Jour. Am. Chem. Soc. *44*, 1382 (1922).

(SO_3H) on the potential of anthraquinone when already sulfonated. Also, Clark in some work as yet unpublished has measured the potentials of certain indophenols, thiazines and suffonated indigos which should be interesting for comparison with this. Considerable data on the free energy of *ionization* of substituted acids has been calculated and compiled by Derick[16] showing the effect of various groups on the free energy of that type of reaction which seems to be different from their effect on the free energy of reduction.

[16] Derick, Jour. Am. Chem. Soc. *33*, 1174 (1911).
ibid., *34*, 74, (1912).

EXPERIMENTAL PART

Plan of the Work

The reduction of quinone in acid solutions may be expressed by the electro chemical equation[17]

$$C_6H_4O_2 + 2H^+ 2(e) \leftrightarrows C_6H_4(OH)_2$$

to which the familiar equation of Peters' applies,

$$\pi = \pi_0 + .05911 \log [H^+] + \frac{.05911}{2} \log \frac{[Q]}{[QH_2]} \qquad (1)$$

$$\pi_0 = \pi - .05911 \log [H^+] - \frac{.05911}{2} \log \frac{[Q]}{[QH_2]} \qquad (2)$$

where π is the observed potential and π_0, the normal potential, i.e., the potential when the ratio of the concentrations (or more precisely the activities) of the oxidized to the reduced forms is unity and the activity of the hydrogen ion is also unity. It is a measure of the work necessary to transform one mole of quinone from the oxidized to the reduced state and shows the intrinsic tendency of the compound to pass from one form to the other. $[Q]$ and $[QH_2]$ are respectively the concentrations of the oxidized and reduced forms, and $[H^+]$ that of the hydrogen ion.

The substituted quinones and hydroquinones were dissolved in HCl buffers of which the hydrogen electrode potential had been carefully determined, and measured quantities of titanous chloride or potassium dichromate were added from a burette, the potentials of the mixture being observed after the addition of each increment. Thus in one titration the potential was recorded for 15 to 20 different concentration ratios of quinone to hydroquinone. The normal potentials were then calculated from equation (2).

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[17] Conant *et al.* have extended this equation to include the potentials for reactions in alkaline solutions. The reaction is different in alkaline solution since hydroquinone behaves as a very weak dibasic acid (K_1 about 10^{-10}), and the reaction may be represented by $C_6H_4O_2 + 2(e) = C_6H_4O_2^{=}$ in which case the potential is independent of the hydrogen ion concentration. Conant's more general equation reduces to that of Peter's whenever the ionization of the hydroquinone becomes negligible, as is the case in all acid solutions, amounting to one part per thousand in a neutral solution or one part in 10^{10} parts in this work.

The cells measured may be represented as follows:

$$\longrightarrow$$

$$\overset{-}{\mathrm{Hg}}\underset{a}{—}\mathrm{HgCl—sat.\ KCl}\underset{b}{—}\left\{\begin{matrix} Q+QH_2\ (y \text{ moles}) \\ H^+(x \text{ moles})\end{matrix}\right\}\underset{c}{—}\overset{+}{\mathrm{Pt}} \qquad (A)$$

$$\longleftarrow$$

$$\overset{+}{\mathrm{Hg}}\text{—}\mathrm{HgCl—sat.\ KCl}\underset{b}{—}\left\{\begin{matrix} H^+(x \text{ moles})\end{matrix}\right\}\underset{d}{—}H_2\,\underset{1\text{ atmosphere}}{\overset{-}{\mathrm{Pt}}} \qquad (B)$$

where x varies from .1 to .2 molar and y from .001 to .003 molar. Subtracting the value of B from that of A eliminates the calomel cell and also any liquid junction potential[18] and gives the value of c against d, the pole of c being positive for data herein recorded, i.e., it gives the value of the combination

$$\overset{+}{\mathrm{Pt}}—\left\{\begin{matrix} Q+QH_2\ (y \text{ moles}) \\ H^+(x \text{ moles})\end{matrix}\right\}—\left\{ H^+(x \text{ moles}) \right\}—H_2\overset{-}{\mathrm{Pt}} \qquad (C)$$

The above precedure is equivalent to performing the operation $-.05911 \log H^+$ in equation (2). It therefore at one and the same time corrects to unit hydrogen ion activity and refers the value of the quinone cell to the standard of the normal hydrogen electrode taken as zero.

The potentials as observed together with the steps of the calculations of the normal potentials are recorded in part in tables I to VI. The constancy of the values of π_0 when measured for different concentrations together with additional data given below shows the validity and precision of the method. Table VII summarizes the influence of each substituent group on the free energy of reduction of the quinone nucleus. A discussion of this data will be given after the validity and precision of the method is discussed.

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[18] The arrows indicate the direction of the current outside the cells. It is true that b differs in combination A by having .003 molar quinone on one side, but the current carried by such a weak electrolyte as hydroquinone in acid solution is entirely negligible in hydrochloric acid solutions.

TABLE I, HYDROQUINONE

Electrometric titration of 20 mg. hydroquinone in 75 cc. M/5 HCl by potassium dichromate of the same acidity. Potential of Combination B= —.2907. Change of hydrogen electrode potential due to the removal of H ion=.0009 for 100% oxidation. End point=17.70 cc.

c.c. Oxidizing solution	% Oxidized	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change (B)	A–B	$\frac{.0591}{2}\log$ (Q)/(QH_2)	π_0 Normal potentials
2.00	11.3	$.3812_5$	$—.2908_0$	$.6720_5$	—.0264	$.6984_5$
3.00	16.95	$.3875_5$	$—.2908_5$	$.6784_0$	—.0204	$.6988_0$
4.00	22.6	.3923	$—.2909_0$	$.6832_0$	—.0158	.6990
5.00	28.2	.3961	$—.2909_5$	$.6870_5$	—.0120	6990_5
6.00	33.9	$.3994_5$	$—.2910_0$	$.6904_5$	—.0084	$.6988_5$
7.00	39.55	.4024	$—.2910_5$	$.6934_5$	$—.0054_5$	.6989
8.00	45.2	$.4055_5$	$—.2911_0$	$.6966_5$	—.0025	$.6991_5$
9.00	50.8	$.4083_5$	$—.2911_5$	.6995	.0004	.6991
10.00	56.5	$.4110_5$	$—.2912_0$	$.7022_5$	$.0033_5$	.6989
11.00	62.15	$.4140_5$	$—.2912_5$	.7053	.0064	.6989
12.00	67.8	$.4172_5$	$—.2913_0$	$.7085_5$	$.0095_5$	.6990
13.00	73.4	.4206	$—.2913_5$	$.7119_5$	.0130	$.6989_5$
14.00	79.1	$.4246_5$	$—.2914_0$	$.7160_5$	.0171	.6989
15.00	84.7	.4295	$—.2914_5$	$.7209_5$	.0220	$.6989_5$
16.00	90.4	.4361	$—.2915_0$	.7276	.0289	.6987
17.00	96.0	.4477	$—.2915_5$	$.7392_5$	.0408	$.6984_5$

Average of normal potentials between 15 and 70%=.6990
Maximum deviation between 15 and 70%=.0002
Average deviation between 15 and 70%=.0001

TABLE II, CHLORQUINONE

Electrometric titration of 22 mg. chlorquinone in 100 cc HCl by titanous chloride of the same acidity. Potential of Combination B = —.2975. Change of hydrogen electrode potential due to removal of hydrogen ion=.0006 for 100% reduction. End point=16.2 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}\log (Q)/(QH_2)$	π_0 Normal potentials
2.00	12.3	.4398	—.2975$_5$	.7373$_5$	.0252	.7121$_5$
3.00	18.5	.4340	—.2976	.7316	.0190	.7126
4.00	24.7	.4293	—.2976$_5$	.7269$_5$	.0143	.7126$_5$
5.00	30.8	.4253	—.2977	.7230	.0104	.7126
6.00	37.0	.4217$_5$	—.2977	.7194$_5$	.0068	.7126$_5$
7.00	43.2	.4183$_5$	—.2977$_5$	.7161	.0035	.7126
8.00	49.4	.4152	—.2978	.7130	.0003	.7127
9.00	55.6	.4119	—.2978$_5$	.7097$_5$	—.0029	.7126$_5$
10.00	61.7	.4086	—.2978$_5$	.7064$_5$	—.0061	.7125$_5$
11.00	67.9	.4049$_5$	—.2979	.7028$_5$	—.0096	.7124$_5$
12.00	74.1	.4011	—.2979$_5$	.6990$_5$	—.0135	.7125$_5$
13.00	80.3	.3964$_5$	—.2980	.6944$_5$	—.0181	.7125$_5$
14.00	86.4	.3909	—.2980	.6889	—.0237	.7126

Average of normal potentials between 15 and 70%=.7126
Maximum deviation between 15 and 70%=.0001$_5$
Average deviation between 15 and 70%=.0000$_5$

TABLE III, TOLUQUINONE

Electrometric titration of 13 mg. toluquinone in 50 cc HCl by titanous chloride of the same acidity. Potential of combination B = —.3013. Change of hydrogen electrode potential due to removal of hydrogen ion = .0010 for 100% reduction. End point = 38.7 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}\log (Q)/(QH_2)$	π_0 Normal potentials
3.90	10.1	.3721	—.3014	.6735	.0280	.6454
5.90	15.25	.3661	$-.3014_5$	$.6675_5$	.0220	$.6455_5$
7.90	20.4	.3616	—.3015	.6631	.0175	.6456
9.90	25.6	.3578	$-.3015_5$	$.6593_5$	.0137	$.6456_5$
11.90	30.8	.3544	—.3016	.6560	.0104	.6456
13.90	35.9	.3514	$-.3016_5$	$.6530_5$	.0074	$.6456_5$
15.90	41.1	.3485	—.3017	.6502	.0046	.6456
17.90	46.2	.3458	$-.3017_5$	$.6475_5$	$.0019_5$	.6456
19.90	51.4	.3430	—.3018	.6448	—.0007	.6455
21.90	56.6	.3402	$-.3018_5$	$.6420_5$	—.0034	$.6454_5$
23.90	61.7	.3374	—.3019	.6393	—.0061	,6454
25.90	66.9	.3343	$-.3019_5$	$.6362_5$	—.0090	$.6452_5$
27.90	72.1	.3312	—.3020	.6332	—.0122	.6454
29.90	77.3	.3274	$-.3020_5$	$.6294_5$	—.0157	$.6451_5$
31.90	82.4	.3232	—.3021	.6253	—.0198	.6451

Average of normal potentials between 15 and 70% = .6455
Maximum deviation between 15 and 70% = $.0002_5$
Average deviation between 15 and 70% = .0001

TABLE IV, THYMOQUINONE

Electrometric titration of 10 mg. thymoquinone in 50 cc HCl by titanous chloride of the same acidity. Potential of combination B =—.3013. Change of hydrogen electrode potential due to removal of hydrogen ion=.0005 for 100% reduction. End point=32.2 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}\log$ (Q)/(QH$_2$)	π_0 Normal potentials
5.00	15.55	.3078$_5$	—.3014	.6092$_5$	.0217$_5$	.5875
7.00	21.8	.3028	—.3014	.6042	.0164	.5878
9.00	28.0	.2986	—.3014$_5$	.6000$_5$	.0121	.5879$_5$
11.00	34.2	.2948	—.3014$_5$	.5962$_5$	.0084	.5878$_5$
13.00	40.4	.2912	—.3015	.5927	.0050	.5877
15.00	46.6	.2880	—.3015$_5$	.5895$_5$	.0017$_5$	.5878
17.00	52.8	.2847	—.3015$_5$	.5862$_5$	—.0014	5876$_5$
19.00	59.0	.2813$_5$	—.3016	.5829$_5$	—.0047	.5876$_5$
21.00	65.2	.2778	—.3016	.5794	—.0081	.5875
23.00	71.4	.2740$_5$	—.3016$_5$	.5757	—.0117	.5874
25.00	77.6	.2694$_5$	—.3017	.5711$_5$	—.0160	.5871$_5$
27.00	83.9	.2640$_5$	—.3017	.5657$_5$	—.0211	.5868$_5$

Average of normal potentials between 15 and 70%=.5877
Maximum deviation between 15 and 70%=.0002$_5$
Average deviation between 15 and 70%=.0001

TABE V, P-XYLOQUINONE

Electrometric titration of 13 mg. p-xyloquinone in 75 cc HCl by titanous chloride of the same acidity. Potential of combination B = —.2907. Change of hydrogen electrode potential due to removal of hydrogen ion =$.0003_3$ for 100% reduction. End point=18.4 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}\log$ (Q)/(QH_2)	π_0 Normal potentials
2.10	11.4	$.3258_5$	—.2907	$.6165_5$	.0263	$.5902_5$
3.00	16.3	$.3202_5$	—$.2907_5$	.6110	.0210	.5900
4.00	21.8	.3157	—$.2907_5$	$.6064_5$	.0164	$.5900_5$
5.00	27.2	.3119	—.2908	.6027	.0126	.5901
6.00	32.6	$.3084_5$	—.2908	$.5992_5$	.0093	$.5899_5$
7.00	38.0	$.3054_5$	—$.2908_5$	.5963	.0063	.5900
8.00	43.5	.3024	—$.2908_5$	$.5932_5$	$.0033_5$	5899
9.00	48.9	.2998	—.2909	.5907	.0006	.5901
10.00	54.3	$.2969_5$	—.2909	$.5878_5$	—.0022	$.5900_5$
11.00	59.8	.2940	—.2909	.5849	—.0051	.5900
12.00	65.2	.2910	—.2909	.5819	—.0081	.5900
13.00	70.7	.2877	—$.2909_5$	$.5786_5$	—.0113	$.5899_5$
14.00	76.1	$.2839_5$	—$.2909_5$	.5749	—.0149	.5898
15.00	81.5	$.2797_5$	—$.2909_5$	.5707	—.0190	.5897
16.00	86.9	.2744	—.2910	.5654	—.0243	.5897

Average of normal potentials between 15 and 70%=.5900
Maximum deviation between 15 and 70%=.0001
Average deviation between 15 and 70%=$.0000_5$

TABLE VI, m- DIMETHOXYQUINONE

Electrometric titration of 15 mg. dimethoxy quinone in 75 cc. M/5 HCl by titanous chloride of the same acidity. Potential of combination B=—.2907,. Change in hydrogen electrode potential due to removal of hydrogen ion=.00034 for 100% reduction. End point=15.0 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}\log (Q)/(QH_2)$	π_0 Normal potentials
2.00	13.3	$.2475_5$	—$.2907_5$	.5383	$.0240_5$	$.5142_5$
3.00	20.0	.2410	—$.2907_5$	$.5317_5$	.0178	$.5139_5$
4.00	26.7	$.2361_5$	—.2908	$.5269_5$	.0130	$.5139_5$
5.00	33.3	$.2322_5$	—.2908	$.5230_5$	.0089	$.5141_5$
6.00	40.0	$.2284_5$	—$.2908_5$	.5193	.0052	.5141
7.00	46.6	$.2249_5$	—$.2908_5$	.5158	$.0017_5$	$.5140_5$
8.00	53.4	.2213	—.2909	.5122	—$.0017_5$	$.5139_5$
9.00	60.0	.2178	—.2909	.5087	—.0052	.5139
10.00	66.7	.2140	—$.2909_5$	$.5050_5$	—.0089	$.5139_5$
11.00	73.4	$.2099_5$	—$.2909_5$	.5009	—.0130	.5139
12.00	80.0	.2050	—$.2909_5$	$.4959_5$	—.0178	$.5137_5$
13.00	86.7	$.1992_5$	—.2910	$.4902_5$	—$.0240_5$	.5143
14.00	93.3	$.1895_5$	—.2910	$.4805_5$	—.0338	$.5143_5$

Average of normal potentials between 15 and 70%=.5140
Maximum deviation between 15 and 70%=$.0001_5$
Average deviation between 15 and 70%=.0001

TABLE VII

NORMAL POTENTIALS OF SOME QUINONE DERIVATIVES SHOWING EFFECT OF SUBSTITUTION

Substance	(A)	(B) corrected for acidity change at mid-point	π_0	Average π_0	log K_0	—ΔF of reduction Kilojoules
m-Dichlorquinone	.4299	—.2909	7208			
oxidized	.4302	—.2909	.7211	$.7209_5$	24.40	139.1
Bromquinone	.4241	—.2909	.7150			
reduced	.4243	—.2909	.7152			
Brom Hydro-				.7151	24.19	138.0
quinone	$.4240_5$	$—.2909_5$	.7150			
oxidized						
Chlorquinone	$.4199_5$	$—.2921_5$	.7121			
reduced	.4148	—.2978	.7126	.7123	24.10	137.5
Chlorhydro-	$.4212_0$	$—.2909_5$	$.7121_5$			
quinone						
oxidized						
Quinone	$.3978_0$	$—.3017_0$	.6995			
reduced	$.4009_5$	—.2979	$.6988_5$	.6990	23.65	
	.4079	$—.2908_5$	$.6987_5$			
Hydroquinone	$.4078_5$	$—.2911_5$	.6990			134.9
oxidized	$.4078_5$	$—.2911_5$	.6990	.6991	23.65	
	.4014	—.2980	.6994			
Toluquinone*	$.3438_5$	$—.3017_5$	.6456			
reduced	$.3437_5$	$—.3017_5$	.6455			
	.3471	—.2978	.6449	.6454	21.84	124.6
	$.3546_5$	$—.2908_5$	.6455			
p-Xyloquinone*	$.2991_5$	—.2909	$.5900_5$	.5900	19.96	113.9
reduced	.2991	—.2909	.5900			
p-Thymoquinone	$.2861_5$	$—.3015_5$	.5877			
reduced	.2859	—.3016	.5875	.5876	19.88	113.4
Dimethoxy-	$,2231_5$	$—.2908_5$	.5140	.5139	17.39	99.2
quinone	$.2229_5$	$—.2908_5$	.5138			
reduced						
Napthaquinone	$.1789_5$	—.2909	$.4698_5$	.4699	15.91	90.7
reduced	.1791	—.2909	.4700			

*The author regrets that the original article of Biilman on "L'hydrogenation des quinhydrones" referred to by Sorensen (ref. p. 1), as "dans l'ecret de fête (Universitites Festskreft)" did not come to her attention through its subsequent publication in Annals re Chemie *15*, 109 (1921), until after this work was ready for the press. His value for toluquinone is identical with that obtained by this method, .6456, but that for xyloquinone varies, being .5960. It is possible that it may be an isomer of the compound used here as the difference is larger than the error of either method.

Discussion of the Method

Validity

It is interesting to examine the validity of this method from the theoretical point of view Unless this is done the first tendency is to question whether the potential measured is really that of the organic material under examination or that due to the inorganic titrating agent as was done by Luther. Assuming for the moment that the charge on the electrode is that which would be imparted by the concentrations of titanous and titanic ions present, we must then ask ourselves what determines this ratio of titanous to titanic ions. The only possible answer that can be given is that it is due to the presence of quinone and hydroquinone and their intrinsic tendencies to pass from one state to the other. That is, a reaction will not reach equilibrium until the E.M.F. set up by one set of components (E_1) is equal to that of the other (E_2) where

$$E_1 = .05911 \log \frac{(Ti^{++++})}{(Ti^{+++})} K_t, \text{ and } E_2 = \frac{.05911}{2} \log \frac{(\underset{\sim}{Q}) \times (H^+)^2}{\underset{\sim}{Q}H_2} K_2$$

In other words, if true equilibrium is reached all the component potentials must be equal. Therefore, the potentials as measured at equilibrium are those due to the concentrations of quinone and hydroquinone which are at the same time equal to those for the concentrations of titanous and titanic ions present.[19] The question therefore resolves itself into determining whether or not true equilibrium is reached. What the mechanism is by which the charge is acquired by the electrode need not concern us here for the potential is in any case a measure of the intrinsic tendency of the compound to pass from the oxidized to the reduced state and vice versa. Even if the charge is conveyed to the electrode through the agency of the titanium or some other ion, the magnitude of that charge must be a property of the organic substance present.

Aside from the considerations above, this method can be valid only if the volume of titrating agent added can be used to calculate the true concentrations of the oxidized and reduced forms at equilibrium, i.e.,

$$\text{if} \quad \frac{(O)}{(R)} = \frac{a_p}{A_e - a_p} \tag{4}$$

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[19] Could we know the exact concentrations of the titanous and titanic ions, the same titration would serve to calculate the normal potential for Ti++++–Ti+++.

where (O)=the concentration of the oxidized form at equilibrium,
(R)=the concentration of the reduced form at equilibrium,
a_p=cc. of the reducing agent added at any point,
A_e=cc. of the reducing agent required to reach the end point.

This is never absolutely true for a reaction that reaches equilibrium instead of proceeding to completion, but it may be true within an error entirely negligible if the titrating agent is properly chosen.

For example, in a reaction of the type $A^\circ + B^+ \leftrightarrows A^+ + B^\circ$ (5) where A° is the reducing agent, there will be one mole of A° converted to the oxidized state for every mole of B° formed, at every point of the reaction.

$\therefore$ at any given point $b^\circ = a^+ = a_p - a^\circ$ (6)
and at the end point $B^\circ = A^+ = A_e - A^\circ$ (7)
where b°=moles of the substance reduced at any given point,
a^+=moles of titrating agent oxidized at any given point,
a_p=moles titrating agent added at any given point,
a°=moles titrating agent left in the reduced state at any given point,
B°=moles of substance reduced at end point,
A^+=moles of titrating agent oxidized at end point,
A_e=moles of titrating agent added to reach end point,
A°=moles of titrating agent left in reduced state at end point.

$$\therefore \frac{b^\circ}{B^\circ} = \frac{a_p - a^\circ}{A_e - A^\circ} \qquad (8)$$

But $B^\circ = B_s - B^+$ (9)

(B_s=moles at the start or total moles of the substance titrated.)

$\therefore$ If B^+, the amount of substance left unchanged (in the oxidized state) at the end point, is negligible in comparison to B_s, (the total quantity), then equation (8) becomes

$$\frac{b^\circ}{B_s} = \frac{a_p - a^\circ}{A_e - A^\circ} \qquad (10)$$

and if at all points in the titration the reducing agent that has been added can be considered to be in the oxidized form, i.e., if a° and

A° are negligible in comparison with a_p and A_e, then it follows that

$$\frac{b^o}{B_s} = \frac{a_p}{A_e} - \text{ or} \tag{11}$$

$$\frac{b^o}{B_s - b^o} = \frac{a_p}{A_e - a_p} \tag{12}$$

which is the same as equation (4),

$$\frac{(\mathrm{O})}{(\mathrm{R})} = \frac{a_p}{A_e - a_p}$$

Thus the problem for any system resolves itself into determining in how far the quantity of reducing, agent added at any time, can be considered to be in the oxidized form, and how completely the material being titrated is converted to the reduced form when the end point is reached, i.e., how nearly the end point and stoichiometric point coincide. This may be determined either from a knowledge of the equilibrium constants for each substance or from their electrometric titration curves.

$$\text{Since } \frac{A^+ \times B}{A \times B^+} = \frac{K_a}{K_B} = K_{\text{equilibrium}} \tag{13}$$

for varying stages of the titration from 0.1 per cent to 99.9 per cent reduction

$$\frac{B}{B^+} = 10^3 \text{ to } 10^{-3} \tag{14}$$

$$\text{therefore } \frac{A^+}{A} = K_{\text{equilibrium}} \times 10^{\pm 3} \tag{15}$$

In order that the error (i.e., the amount of A left in the reduced form) should not exceed 1 part per 1000, i.e., $A^+/A = 1000/1$, it follows that

$$K_{\text{equilibrium}} \times 10^{\pm 3} = 10^3 \tag{16}$$

or $K_{eq.} = 10^6$.

That is, the ratio K_a/K_b must be at least equal to 10^6. In the case of titanium and quinone $K_B = 10.^{23.65}$ and $K_a = 10^{-1.85}$, the ratio being 10^{25}, which means that all the titanium added can be considered to be in the titanic form within an error of 1 part in 10^{22} parts over a range of 0.1 per cent to 99.9 per cent reduction. Further, it is important for practical considerations to choose a reducing agent such that this ratio is as large as possible since the ratio $\Delta\pi/\Delta v$ must rise to a sharp maximum in order to secure an accurate experimental end point.

Experimental Proof of Validity

It was shown above from theoretical considerations that the question as to whether the potentials measured in the presence of a secondary substance are those of the specific components under examination resolves itself into determining whether or not true equilibrium is reached. The criteria outlined by Luther, in criticizing the use of secondary materials are in reality criteria of equilibrium. They have all been rigidly met in this work, for,—

(1) The potentials obtained were constant and reproducible over a wide range of concentrations as shown by the constancy of π_0 (tables I-VI) and its reproducibility in different titrations (table VII).

(2) Moderate anodic and cathodic polarizations had no effect.

(3) The same potentials were obtained with electrodes of pure gold, gold-plated platinum, and platinum, although the first two gave the sharpest potentials and came to equilibrium more quickly.

(4) The normal potential of quinone-hydroquinone obtained by this method (.6990±.0003), is in close accord with Nelson and Granger's[20] value determined by the method of pure mixtures and also with Biilmann's[21] value (.6990±.0002) for the quinhydrone electrode. Nelson and Granger did not refer their results to the normal hydrogen electrode, but taking Nelson and Beegle's value of .4094 as the most likely for combination B in their work, the value .6989±.0014 is obtained. The value of Haber and Russ[22] is somewhat higher, .745, which is probably due partly to the fact that they worked in alcoholic solutions[23], and partly due to their assuming complete dissociation of quinhydrone in saturated solution.

[20] Granger and Nelson, ref. 2.

[21] Biilmann Annales de Chimie 9 serie V *16*, 321 (1921).
This work came to the notice of the author on July 28, 1922, after this paper was almost completed.

[22] Haber and Russ, ref. 1.

[23] The work of Conant seems to indicate that the potential is dependent on the nature of the solvent.

Besides meeting these criteria of Luther, a still more conclusive test was applied to prove that true equilibrium was obtained and to demonstrate that the titrating agent or catalyst had no effect whatsoever on the normal potentials, namely that of approaching the equilibrium from both sides, using a reducing agent of low normal potential in one case ($TiCl_3$) and an oxidizing agent of high normal potential in the other ($K_2Cr_2O_7$). This was done for three systems with the results shown in table VIII.

TABLE VIII

Quinone reduced by $TiCl_3$	.6990*
Hydroquinone oxidized by $K_2Cr_2O_7$	.6991
Chlorquinone reduced by $TiCl_3$	$.7123_5$
Chlorhydroquinone oxidized by $K_2Cr_2O_7$	$.7121_5$
Bromquinone reduced by $TiCl_3$	.7151
Bromhydroquinone oxidized by $K_2Cr_2O_7$	.7150

Such concordance of results is excellent proof that equilibrium is attained and eliminates any idea that the titrating agent can influence the normal potentials in any way. Conant[24] and his co-workers state that they have shown the validity of this method by comparing it with the method of mixtures but their value for the sodium salt of B anthraquinone sulfonic acid determined by the electrometric method differs from that by his method of mixtures by .011 volts in one case and .015 volts in another, while the above differs by .0001 and .0002 volts.

Sources of Error

The most obvious and unavoidable experimental errors likely to occur in this method are error in reading the burette (.02cc), that due to varying amounts of titrating solution clinging to the tip of the burette (.03cc), and an error in determining the end point. Table IX was constructed to show the effect of these errors on the potentials observed at different stages of the titration, taking an error of .05 cc on a 30 cc titration, or less than 2 parts per 1000 for the combined error from the first two sources and an error of .2 cc for 30 cc titration (or .1 cc for a 15 cc titration) as a likely error for the end point determination. Column G gives the probable error of the two, i.e., the square root of the sum of the squares of each error. The same is shown graphically in figure I where curve A shows the combined effect of the error of the hanging drop and of reading the burette. Curve B shows the most likely error in determining the end point, and curve C the probable error from both sources. Since the effect of the end point error may become very pronounced in the later stages of the titration, only those values that correspond to a range of 15 to 70 per cent reduction or oxidation corresponding to an error limit of ±0.3 mv. from these sources have been included in determining the average values of π_0.

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[24] Conant *et al.*, ref. 15.

*Biilmann's value for quinone by quinhydrone electrode=.6990. Granger and Nelson's value (saturated solutions)=.6989.

TABLE IX

Calculation of effect of error of titration and end point on results. Assume end point error of .1 cc in 15.0 cc (.2 in 30.0) and error from reading burette and hanging drop .05 cc. in 30.0 cc.

A	B	C	D	E	F	G
% reduction	% reduction with error due to reading burette and hanging drop	Difference in $\frac{.05911}{2}\log$ (Q)/(QH$_2$) due to error in B	% reduction with end point error	Difference in $\frac{.05911}{2}\log$ (Q)/(QH$_2$) due to error in D	Maximum error C+E	Probable error $\sqrt{C^2+E^2}$
5.0	5.17	.0005	5.03	.000079	.00060	.00050
10.0	10.17	.0003	10.07	.000095	.00040	.00031
15.0	15.17	.0002½	15.10	.000100	.00030	.00021
20.0	20.17	.0002	20.14	.000110	.00034	.00020
30.0	30.17	.0001½	30.20	.000121	.00030	.00019
40.0	40.17	.0001	40.27	.000145	.00027	.00017
50.0	50.17	.0001	50.34	.000174	.00028	.00019
60.0	60.17	.0001	60.42	.00022	.00032	.00024
70.0	70.17	.0001½	70.47	.00027	,00042	.00031
80.0	80.17	.0002	80.54	.00044	.00064	.00049
85.0	85.17	.0002½	85.54	.00054	.00074	.00057
90.0	90.17	.0003	90.63	.00093	.00123	.00097
95.0	95.17	.0005	95.67	.00194	.00244	.00201

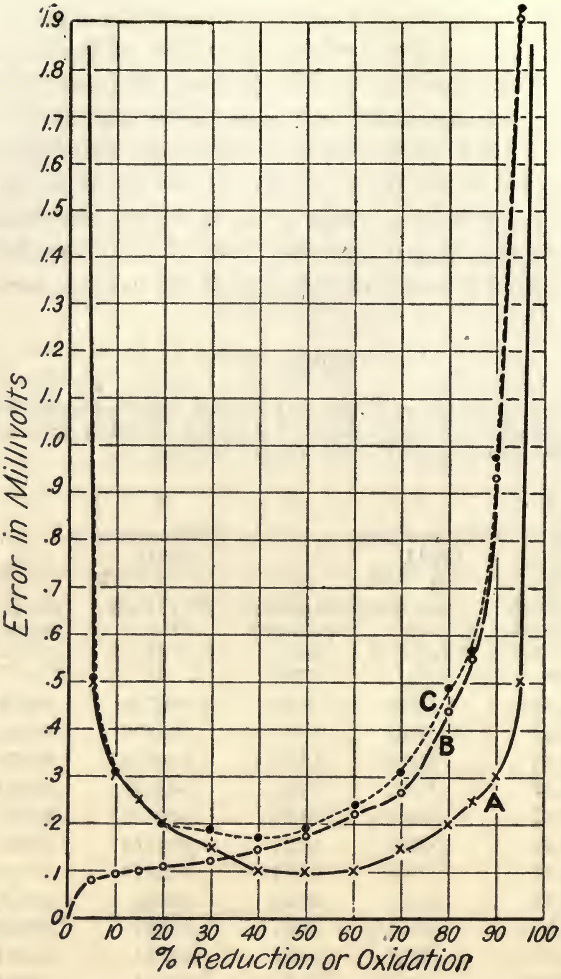

Figure I

In order that the method might be made as precise as possible a correction was introduced which has not been taken account of by any previous investigator, namely, for the change of acidity due to the reaction itself as indicated by the equations:

$$C_6H_4O_2+2H^{+}+2Ti^{+++}=C_6H_4(OH)_2+2Ti^{++++} \quad (3)$$

$$3C_6H_4(OH)_2+8H^{+}+Cr_2O_7^{=}=3C_6H_4O_2+2Cr^{+++}+7H_2O \quad (4)$$

$2\frac{2}{3}$ moles of hydrogen ion being removed per mole of hydroquinone when dichromate is used and 2 when titanous chloride is used. This correction is called that of acidity change to distinguish it from the other larger correction of acidity represented by B(tables I-VI). It is positive for equations (3) and (4) and amounts in some of this work to one millivolt for 100 per cent reduction or oxidation and is distributed proportionally in column 4.[25] In the titrations of Conant *et al*[26], for 0.0407 M hydrogen ion it amounts to as much as 4.1 millivolts and is probably one of the causes for the variation of the slopes of their curves (i.e., π_0 drifts) which they attribute to the formation of quinhydrone.

That any error due to the possible formation of quinhydrone is entirely negligible in the dilute solutions used in this work can be shown by calculation from its dissociation constant (.263) which has been determined independently by Granger and Nelson[27] and by Sorenson[28] and his collaborators. The error in the observed potentials that would be caused by the association of quinone and hydroquinone to form quinhydrone is expressed by the equation,

$$\frac{.05911}{2} \log \frac{(Q)}{(QH_2)} - \frac{.05911}{2} \log \frac{(Q)-x}{(QH_2)-x} \qquad (17)$$

where x=moles associated quinhydrone.

This correction would be a maximum toward the ends of the titration where either (Q) or (QH_2) is small and would decrease to zero at 50 per cent reduction where (Q)=(QH_2). To determine how great the maximum effect can be in this work we should calculate the value of x at 20 per cent and 80 per cent reduction. If x=the moles of associated quinhydrone per liter, its value at 20 per cent or 80 per cent reduction in a .002 molar solution would be obtained from the following equation,

$$.263 = \frac{(QH_2)\times(Q)}{(Qh)} = \frac{(.0004 - x)\ (.0016 - x)}{x} \qquad (18)$$

where (Qh)=conc. of quinhydrone.

Solving, x is found to equal .0000024 moles per liter. Substituting this value in equation (17) the correction on the potential for this error would be

$$\frac{.05911}{2} \log \frac{.0016}{.0004} - \frac{.05911}{2} \log \frac{,0016 - .0000024}{.0004 - .0000024} \qquad (19)$$

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[25] This corection is calculated as follows:

$$E_1 - E_2 = .05911 \log \frac{1}{(H+)} - .05911 \log \frac{1}{(H+^1)}$$

where (H+)=moles hydrogen ion at start (E_1—E_2 the correction). ($H+^1$=moles hydrogen ion at end of titration.

[26] Conant, loc. cit., p. 1391.

[27] Granger and Nelson, ref. 2.

[28] Sorensen. Annales de Chimie, 9 serie, *16*, 283 (1921).

or only 0.06 mv., an amount entirely negligible as it could not affect the average over this range of concentrations by more than 0.03 mv. If it can be assumed, as is probable, that the dissociation constants of the other quinhydrones are of the same order of value as that of quinhydrone itself, then the influence of this factor is eliminated. Moreover, no trace of color due to a quinhydrone was ever observed and the constancy of the value of π_0 obtained for the various quinone derivatives proves that the error from this source is entirely negligible and confirms the above calculation. In the light of this work it seems improbable that the drifts of ±2—±10 mv. in the titrations of Conant *et al.* on anthraquinone sulfonic acids can be due to this cause alone, as they suggest.

The precision obtainable is conditioned by the technique and also very largely by the purity of the compounds used. A high degree of purity is necessary because the validity of the whole method rests on the assumption that

$$\frac{(\mathrm{O})}{(\mathrm{R})} = \frac{a_p}{A_e - a_p}$$

If a second reducible substance is present this equality cannot hold unless their reduction potentials are identical or are so widely widely separated that all of one is reduced before the other is attacked. The very fact that component potentials at equilibrium are equal makes it mathematically impossible for the two substances in a mixture to have the same concentration ratio of oxidized to reduced forms, i.e., the same concentration correction, unless their normal potentials are identical. Therefore, the substance with a higher normal potential will have a greater quantity in the reduced form and that of lower normal potential a less quantity in the reduced form than would be indicated by the ratio.

$$\frac{a_p}{A_e - a_p}$$

Obviously, then, for the method to be valid, material of a high degree of purity must be used.

In order to illustrate experimentally the effect of reducible impurities on the potentials obtained two mixtures were titrated, one containing approximately 20 per cent quinone and 80 per cent toluquinone, the other approximately 10 per cent toluquinone and 90 per cent quinone, with the results shown in tables X and XI.

TABLE X, QUINONE WITH 10% TOLUQUINONE AS IMPURITY

Total of 11 mg. in 75 M/5 HCl titrated with titanous chloride of same acidity. Potential of combination B = —.2907. Change in hydrogen electrode potential due to removal of hydrogen ion = .00035 for 100% reduction. End point = 24.2 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}\log (Q)/(QH_2)$	π_0 Normal potentials
3.00	12.4	.4307	—.2907$_5$	.7214$_5$	.0251	.6963$_5$
4.00	16.5	.4264	—.2907$_5$	.7171$_5$	.0208	.6963$_5$
5.00	20.6	.4228$_5$	—.2907$_5$	.7136	.0173	.6963
6.00	24.8	.4196	—.2908	.7104	.0142	.6962
7.00	28.9	.4168	—.2908	.7076	.0115$_5$	.6960$_5$
8.00	33.0	.4141	—.2908	.7049	.0091	.6958
9.00	37.2	.4116	—.2908$_5$	.7024$_5$	.0067	.6957$_5$
10.00	41.3	.4091	—.2908$_5$	.6999$_5$	.0045	.6954$_5$
11.00	45.5	.4067$_5$	—.2908$_5$	.6976	.0023	.6953
12.00	49.6	.4043	—.2908$_5$	.6951$_5$	.0002	.6949$_5$
13.00	53.7	.4018$_5$	—.2909	.6927$_5$	—.0019	.6946$_5$
14.00	57.9	.3995	—.2909	.6904	—.0041	.6945
15.00	62.0	.3967$_5$	—.2909	.6876$_5$	—.0063	.6939$_5$
16.00	66.1	.3937$_5$	—.2909$_5$	.6847	—.0086	.6933
17.00	70.3	.3901$_5$	—.2909$_5$	.6811	—.0110	.6921
18.00	74.4	.3866	—.2909$_5$	.6775$_5$	—.0137	.6912$_5$
19.00	78.5	.3818$_5$	—.2909$_5$	.6728	—.0166	.6894
20.00	82.6	.3759	—.2910	.6669	—.0200	.6869
21.00	86.8	.3687	—.2910	.6597	—.0241$_5$	.6838$_5$
22.00	90.9	.3583	—.2910	.6493	—.0295	.6788

Normal potential at 50% reduction .6949

Drift between 15 and 70% .0042

TABLE XI, TOLUQUINONE WITH 20% QUINONE AS IMPURITY

Total of 10 mg. in 75 cc. M/5 HCl titrated with titanous chloride of same acidity. Potential of combination B= —.2907. Change of hydrogen electrode potential due to removal of hydrogen ion=.00031 for 100% reduction. End point=24.2 cc.

c.c Reducing solution	% Reduction	Observed potentials Combination A	Observed potentials Combination B corrected for acidity change	A–B	$\frac{.05911}{2}$ log (Q)/(QH$_2$)	π_0 Normal potentials
3.00	12.4	.4087	—.2907$_5$	.6994$_5$	.0251	.6743$_5$
4.00	16.5	.4013$_5$	—.2907$_5$	.6921	.0208	.6713
5.00	20.6	.3947	—.2907$_5$	.6854$_5$	.0173	.6681$_5$
6.00	24.8	.3880	—.2908	.6788	.0142	.6646
7.00	28.9	.3817$_5$	—.2908	.6725$_5$	.0115$_5$	.6610
8.00	33.0	.3767$_5$	—.2908	.6675$_5$	.0091	.6584$_5$
9.00	37.2	.3723	—.2908	.6631	.0067	.6564
10.00	41.3	.3686	—.2908$_5$	.6594$_5$	.0045	.6549$_5$
11.00	45.5	.3650	—.2908$_5$	.6558$_5$	.0023	.6535$_5$
12.00	49.6	.3619	—.2908$_5$	.6527$_5$	.0002	.6525$_5$
13.00	53.7	.3590	—.2908$_5$	.6498$_5$	—.0019	.6517$_5$
14.00	57.9	.3561$_5$	—.2909	.6470$_5$	—.0041	.6511$_5$
15.00	62.0	.3534	—.2909	.6443	—.0063	.6506
16.00	66.1	.3505$_5$	—.2909	.6414$_5$	—.0086	.6500$_5$
17.00	70.3	.3478	—.2909	.6387	—.0110	.6497
18.00	74.4	.3448$_5$	—.2909$_5$	.6358	—.0137	.6495
19.00	78.5	.3416	—.2909$_5$	.6325$_5$	—.0166	.6491$_5$
20.00	82.6	.3378	—.2909$_5$	.6287$_5$	—.0200	.6487$_5$
21.00	86.8	.3332	—.2909$_5$	.6241$_5$	—.0241$_5$	.6483
22.00	90.9	.3276	—.2910	.6186	—.0295	.6481

Normal potential at 50% reduction	.6525$_5$
Drift between 15 and 70%	.0213

The values of π_0 in column 7 show the magnitude of the drifts that were caused, 22.0 mv. and 4.4 mv. It is interesting to note that where the substance representing an impurity was of higher normal potential a much greater drift was caused than where it was of lower potential. In the latter case the impurity was reduced so late in the titration that it had only the effect of displacing the end point approximately .5 cc. In both cases, as is shown by figure II where curves I and IV are for pure quinone and toluquinone and II and III for the mixtures, the potentials at first approximate those for the compound of higher normal potential and gradually drift over to those for the other compound. In such cases where a drift is obtained between 15 per cent and 70 per cent reduction, the curves show that it is not an accurate procedure to take the values at 50 per cent reduction as the normal potentials (unless one does not wish to approximate to the precision of this work)[29], as in these instances they differ by 7.0 and 4.0 mv. from the true values. Figure II also illustrates how closely the experimental and theoretical values coincide when the material is sufficiently pure, the dots representing experimental points and the crosses theoretical points as obtained from the Van't Hoff equation.

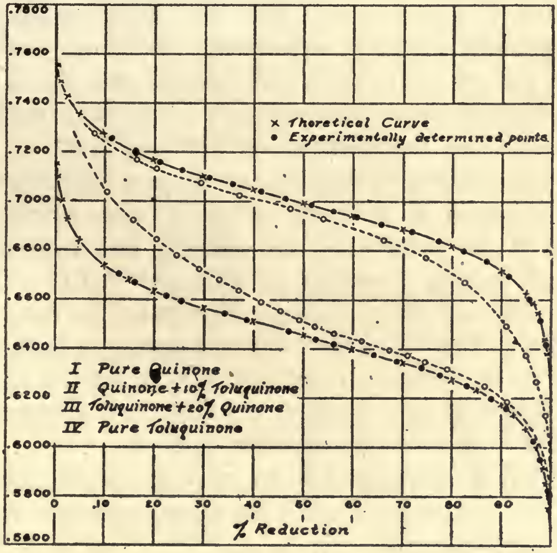

Figure II

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[29] Conant *et al.* believe this procedure sufficiently precise for their purpose. However, work of that precision would not have shown the difference in potential between the chlor and brom compounds and the interesting relation involved therein.

An attempt was made to determine the quantity of dissolved oxygen left in the solution during the titration. The apparatus was arranged as for the electrometric titration, the beaker containing only HCl buffer solution. Nitrogen was bubbled through exactly the same as in the titration. (See procedure). Then a mixture of ferrous amonium sulfate and potassium thiocyanate was introduced by means of a pipette. Nitrogen was again bubbled through and the whole mixture allowed to stand for approximately the same length of time as required for the electrometric titration. At the end of this time the amount of titanous chloride solution was determined which was required to reduce any ferric iron that was formed by the oxygen present. The results showed that usually there was no oxygen present but occasionally there was a slight amount requiring 0.05 cc of the weakest titanium solution, equivalent to displacing the end point .05 cc, which probably accounts for the slightly greater drift in some of these results than in others, a drift of ±.5 mv. occurring occasionally.

It is necessary for precise work that account be taken of the difference between activities and concentrations. Strictly speaking, the Van't Hoff isotherm holds only if Q and QH_2 represent activities. In this particular work, however, since buffer solutions varying only from .1 N to .2 N were used, the concentrations of quinone and hydroquinone can be substituted for their activities, for Sorensen[30] and his co-workers have shown that the ratio of the activities of quinone and hydroquinone is identical to the ratio of their concentrations for solutions of HCl and NaCl of .1 N concentration and varies only slightly (an amount equivalent to a correction of 0.3 mv.) at .2 N, the activities being determined from differences in the solubilities of quinone and hydroquinone in solutions of varying normality of HCl and NaCl. Their work shows the value of the correction[31] that must be made for other concentrations. Obviously then, before titrating in buffer solutions of other salts at different ranges of pH, it will be necessary to determine this difference between activities and concentrations as Sorensen has done by an independent method.

In order that there should be no error due to junction potential, the same type of junction, in fact the same apparatus, was used in

[30] Sorensen (ref. 28).

[31] The correction for this difference in activities and concentrations is, I believe, identical with what some investigators call solubility correction. The different values obtained for normal potentials in solutions of varying hydrogen ion concentration is undoubtedly due to a change of activities of the components in the buffer solutions used.

determining the hydrogen electrode potential of the HCl buffer (Combination B) as in the electrometric titration (Combination A). Thus, subtracting B from A eliminates the value of the junction potential. However, this is the case only if the value of that potential is constant and strictly reproducible. It was found that the ground glass stopper form of junction (see figure IV for description) met this requirement admirably, as well as proving the best known for preventing the interdiffusion of the quinone substances and the KCl of the salt bridge. Its reproducibility is demonstrated by the fact that the same value was obtained for any one buffer on every date used, four buffers being tried each on five different dates. Table XII shows the constancy of this form of junction over a period of ten hours for .2 N HCl.

TABLE XII

Constancy of ground glass stopper junction as shown by value of .2 N HCl against the saturated calomel cell.

1 hr.	**0.29068**
2 hrs.	**0.29069**
3 hrs.	**0.29070**
4 hrs.	**0.29070**
6 hrs.	**0.29070**
10 hrs.	**0.29067**

TABLE XIII

Data Showing Effect of Type of Junction and Reproducibility of Glass Stopper Junction

Glass stopper junction	
initial reading	**.30810**
20 minutes	**.3083½**
40 “	**.3083½**
60 “	**.3083½**
2 hrs.	**.3083½**
Fresh junction with glass stopper	
10 minutes	**.3085**
25 “	**.3083**
45 “	**.3083**
1 hr.	**.3083**
Fresh junction with glass stopper	
20 minutes	**.3083**
40 “	**.3083**
60 “	**.3083**
Loose cotton plug	
10 minutes	**.3094**
15 “	**.3086**
20 “	**.3090**
Capillary junction	
5 minutes	**.3108**
7 “	**.3097**
10 “	**.3084**
Capillary tube with tight cotton plug	
20 minutes	**.3100**
25 “	**.3100**
30 “	**.3100½**
45 “	**.3101**
1 hr.	**.3102**

Other values obtained without aging, with junctions of various forms

.3128	**.3067**
.3116	**.3086**

Table XIII for .1 N HCl demonstrates the reproducibility of the value of the junction when the plug was removed and fresh junctions made, also the fact that different values are obtained with different types of junctions. This difference in value according to the type of junction, the compactness of fixing a cotton plug, and the time of aging, explains, I believe, the varying values that occur in the literature[32] for .1 N HCl against the saturated calomel cell.

Precision

By taking account of the above sources of error and eliminating them as nearly as possible a precision of ±0.2 mv. has been obtained as the average deviation for all the titrations on 12 compounds. (See table XIV). This lends no support to Conant's[33] statement that the errors of the titration method seem to be about 5.0 mv. It also compares favorably with Clark's[34] deviations which in acid solution are ±2.4 mv. for indigo and ±12.0 mv. for methylene blue.

TABLE XIV

MAGNITUDE OF DRIFTS AND AVERAGE DEVIATIONS

15-70%

Substances	*Drift*	*Average Deviation*
Hydroquinone	±.0002	.0001
Quinone	.0003	.0001½
Bromhydroquinone	.0003	.0002
Bromquinone	.0002½	.0001
Chlorhydroquinone	.0003½	.0002½
Thymoquinone	.0002½	.0001
Chlorquinone	.0002½	.0001
Xyloquinone	.0001	.0000½
Napthaquinone	.0005	.0002
Dimethoxyquinone	.0001½	.0001
Toluquiuone	.0002½	.0001

Precision of Method for Pure Compounds=±.0002

Effect of Impurity

10% impurity of lower potential Drift=±.0028

20% impurity of higher potential Drift=±.0188

Deviation at 50% from true value = .0041 and .0071

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[32] Values for 0.1 N HCl in combination (B) (column I), and the values of the saturated calomel cell derived therefrom, using .0612 as the pole potential for 0.1 N HCl (α 92%) (Column II).

I	II	Author
.3100	.2488	Fales and Mudge, Jour. Am. Chem. Soc. *40*, 2443 (1920).
.3094	.2482	Nelson and Beegle, ibid. *42*, 2226 (1920) quoted.
.3111	.2499	Beans and Oakes, ibid. *42*, 2226 (1920).
.3083	.2471	Results with ground glass stopper junction.
....	.2462	Clark, Determination of Hydrogen Ions. Williams and Williams and Wilkins, Baltimore, p. 306.
....	.2458	Michaelis, quoted by Clark, p. 140.

[33] Conant, ref. 15.

[34] Clark, ref. 5.

Also the drifts of π_0 (the deviations over a range of 15 to 70 per cent reduction) are of the same order of value, ±0.3 mv., in this work. Over the same range and also in acid solutions, Clark obtained deviations varying from ±0.3 to ±2.1 mv., and Conant *et al.*[28], using materials of 96, 95, 94, 87, 92, 83 and 56 per cent purity, give deviations of ±1.5 to ±10.0 mv. between 20 and 80 per cent reduction. For this reason they took the value for the normal potential from the curves at 50 per cent reduction instead of the average for many varying concentrations as done herein.

From the above discussion and data it is seen that the electrometric titration method of determining the normal potentials of certain organic compounds is proven to be superior to the method of pure mixtures in that it is exceedingly rapid and free from troublesome determinations of concentrations by analytical means; is equally valid, and may be made sufficiently free from errors to be precise to ±0.2 mv. It can therefore be used quite successfully in a study of the effect of substituent group on the free energy of reversible reductions.

Discussion of Data

With the number of compounds so far investigated it would be unwise to try to formulate any general conceptions or to theorize much concerning the effect of substitutions on the free energy of reduction of a compound. However, even from the data at hand it will be seen that taking quinone as a reference point the free energy of reduction is increased or decreased in general according to the electro positive or electro negative character of the substituted group as would be qualitatively predicted by the rule of Michael. The former causes a decrease in the normal potential and the latter an increase, i.e., it requires a higher hypothetical pressure of hydrogen to reduce the quinone nucleus when it contains an alkyl group and a lower pressure for a halide. See figure III for curves showing this relationship, also table VII. The relative influence of the various groups was found to be in the following order:

m-dichlor> brom> chlor >none>methyl>isopropyl(predicted) >
22 16.1 13.35 0 —53.6 —57.8
p-dimethyl>methyl p-isopropyl>m-dimethoxy>C_6H_4 (naptha
—109.0 —111.4 —184.3 —229.2
quinone).

The figures given are the differences in millivolts between the normal potentials of the substituted quinones and that of quinone.

PLATE 2

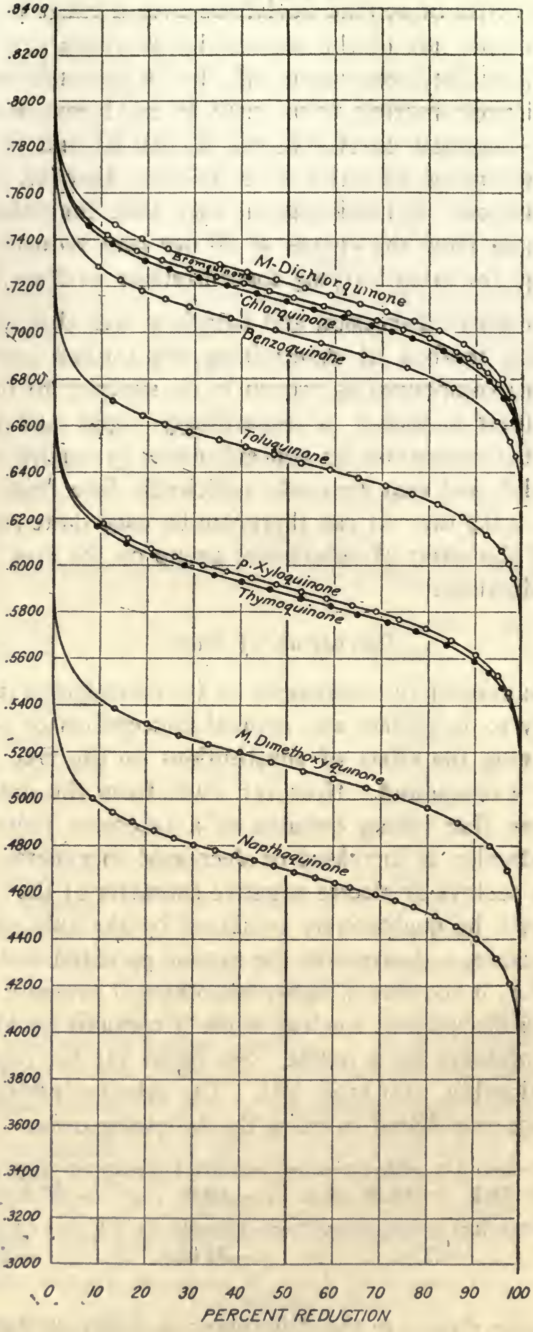

Figure III

On the basis of the positive and negative rule it appears odd that the chlorine atom should offer more resistance to the introduction of hydrogen than does the bromine atom. This reversal of position cannot be due to any experimental error since the same potentials were obtained on reducing the quinones as on oxidizing separate preparations of the hydroquinones, and also since the constancy of π_0 throughout the titrations showed that the compounds were pure. The same anomalous position of the chlor and brom groups has been recorded by Derick[35] in his work on the free energy of ionization of substituted benzoic acids. He finds that when the groups are in the ortho position the order of their effect is Br$>$I$>$Cl, but in the meta position the normal order is maintained Cl$>$Br$>$I.

It is indicated therefore that a space factor must be considered as well as the positive and negative character of the groups. This is also supported by the observation of Kehrman that the introduction of oxime groups in forming oximes of substituted quinones is less influenced by the electronegative character of the groups than by their position. It will therefore be interesting to determine what effect the position of the groups has as revealed by a study of isomeric compounds. Already the work of Conant[36] *et al.* shows that in the sulfonic acids of anthraquinones the substitution of a second sulfonic acid group in the α compound does not increase the potential as much in the 1 5 positions as it does in the 1 8 positions.

It is interesting to note further in this connection that he shows that α SO_3H groups affect the free energy of *ionization* of the hydroanthraquinones, while β SO_3H groups do not, showing as Derick's work does that the free energy of *ionization* is affected by the position of the group.

A comparison of the effect of the substituted groups on the free energy of reduction of quinone with the effect of the same groups on the free energy of ionization[37] of benzoic acid when the groups are in the same relative position, leads one at first to believe that the effect is very different. Alkyl groups appear to have only a very small effect and halide groups a large influence on the free energy of ionization, while in the reduction of the quinone nucleus the reverse appears to be the case. It must be remembered, however, that in the case of ionization the positivity of the alkyl groups is greatly decreased by the presence of the strongly negative COOH group and the negativity of the halides greatly magnified. If, then, for this comparison, we take the value of the COOH group as the reference point in ionizaiton as we take quinone for the reference point in reduction comparisons, we find that the order of substituents is in general the same (the naptha compound being an exception) and the magnitude of the effect not as greatly different as at first supposed. For instance, the order of the groups in the case of ionization is as follows:

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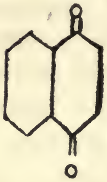
[35] Derick, Jour. Am. Chem. Soc. *34*, 74 (1912).

[36] Conant, *et al.*, ref. 15.

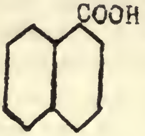
[37] This data is taken partly from Derick's work, Jour. Am. Chem. Soc. *34*, 74 (1912), and partly calculated from the values for K_a in Scudder's tables.

o-Br>o-Cl>o-COOH>C_6H_4>o-CH_3>2, 5, dimethyl>2, 4, dimethoxy.
.466 .455 .425 .129 .069 .064 —.0598

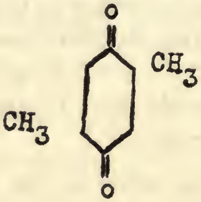
The figures are Derick's place factors.[38] The striking exception, namely, that of the naptha compound, does not invalidate the comparison if one considers the structures of the compounds concerned. In the quinone there are two reacting C=O groups and the C_6H_4 group has a linking in the ortho position to each group, while in napthoic acid there is only one reacting COOH group, and one joining of the C_6H_4 group is relatively far removed. A similar mode of reasoning may be applied to the two dimethyl compounds.



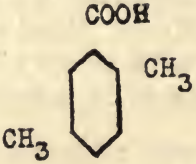
and



In dimethyl quinone



the methyl groups are each ortho to a C=O group and therefore have equal influence, while in dimethyl benzoic acid the two groups



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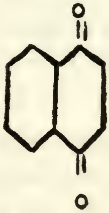
[38] Derick, Jour. Am. Chem. Soc. *33*, 1174 (1911).
Jour. Am. Chem. Soc., *34*, (1912).

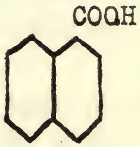
have unequal effect due to their positions being ortho and meta respectively. Possibly for disubstituted compounds comparisons could be made with the terrephthalic acids in place of benzoic acid. Observation of the structural formulae will aid in seeing these relationships.

FREE ENERGY OF REDUCTION

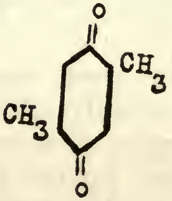
FREE ENFRGY OF IONIZATION



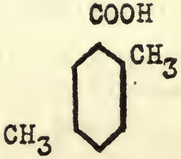
2 ortho linkings
larger effect due to C_6H_4.



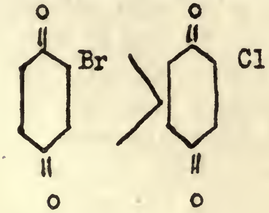
1 ortho and 1 meta linking
effect of C_6H_4 not so large.



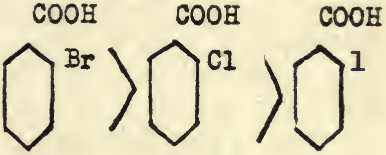
2 ortho linkings
effect of the 2 groups equal.



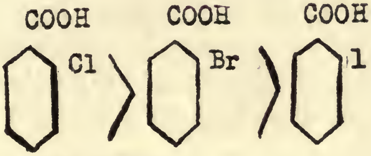
1 ortho group, 1 meta group
effect of the 2 groups not equal.



ortho position



ortho position



meta position

The fact that the effect of the two methyl groups in p dimethyl quinone is almost exactly equal and is additive (the difference in the normal potentials of quinone and toluquinone being .0546, and of toluquinone and p-xylo quinone .0554 volts) would lead one to suspect that the effect of different substituents in a compound will be found to be additive as Derick[38] has shown it to be on the free energy of ionization of substituted aliphatic and benzoic acids. If this is so, it may be predicted from the value for thymoquinone that the value of the isopropyl group alone should be about .0578 volts. But without prediction, it is evident from the above that the magnitude of the influence of substituted groups on the free energy of reduction is influenced by two factors, (1) the positivity or negativity of the group, and (2) its relative position to the reacting group.

It will be interesting to see in how far the relationships for the quinone nucleus hold for other nucleii such as napthaquinone and anthraquinone, that is, whether the ratio between two groups is quantitatively the same in different nuclei and whether any precise definition of positivity and negativity for groups can be given that will hold for all nuclei in oxidation-reduction.

Much work, it is true, has been done in organic chemistry on the influence of groups on certain reactions and explaining that influence according to the positive or negative character of the group. For instance, in regard to the quinone-hydroquinone reaction, Heinrich,[39] referring to the work of Kehrmann, states that the lower the homologue and the more negative the substituents in the molecule, the more easily quinones take up hydrogen and pass into hydroquinones, while the reverse reaction is favored by high molecular weight and the accumulation of positive groups. This explains why a mixture of hydrothymoquinone and benzoquinone rearrange to give thymoquinone and hydrobenzoquinone. Work, however, of the nature recorded herein, where the quantitative value for each compound or group is known will enable one to predict with certainty not only in which direction such reactions will proceed, but, the equilibrium constants being known, just how far any such reaction will proceed to completion. Moreover, it gives a means of distinguishing the intensity and completeness from the velocity of the reaction. This work, therefore, when sufficiently

[39] Heinrich, Theories of Organic Chemistry, p. 163.
Translated by Johnson and Hahn, 1922.
Wiley and Son, New York.

extended should be helpful in explaining many organic reactions and may perhaps modify some of our present ideas that are based on qualitative effects only. For instance, without the quantitative measurement one would not have suspected the relative influence of the chlor and brom groups.

It may even be suggested now that when sufficient data is available the normal potential of compounds together with the known effect of each group may be effective in determining their structure as Derick has shown to be the case with the ionization constants of the substituted acids.

It will be noted that the value of log K_0 is given in table VII for each system, as well as the free energy of reduction in joules. This is the positive exponent of the equilibrium constant when the equation is written in the form

$$\pi_0 = \frac{.05911}{2} \log \frac{(Q)(H^+)^2}{(QH_2)} \,.\, K_0$$

that is $K_0 = \frac{(QH_2)}{(Q)(H^+)^2}$, or when $(H^+)=1$, $K_0 = \frac{(QH_2)}{(Q)}$

The value of the constant shows the ratio of the concentrations of the reduced to the oxidized forms existing in equilibrium with a molal hydrogen electrode. The positive value of the exponent of K_0 (i.e. log K_o) then becomes identical in sign and value with Clark and Zoller's[40] r_H, which is the negative value of the exponent of the hypothetical pressure in atmospheres of gaseous hydrogen in equilibrium with an equimolecular mixture of the oxidized and reduced forms in a molal hydrogen ion solution. They have proposed the use of the symbol r_H in a manner analogous to Sorenson's p_H as a convenient index in biological work of the oxidizing or reducing properties of a material. The thermodynamic constant or log K_0 is suggested here[41] in preference to r_H largely because, as written in this paper, it avoids the troublesome change from negative to positive values, and also because it does not involve the assumption of a hydrogen gas pressure so minute that in many cases its existence is merely hypothetical. Thus for the quinone equilibrium this gas pressure ($10^{-23.65}$ atmospheres) would represent a concentration of only 1.4 molecules of hydrogen in 22.4

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[40] Clark and Zoller, Science N.S. *44*, 557 (1921).
See also Clark, ref. 27, chap. 14, and ref. 5, p. 260, for a discussion of the meaning of r_H.

[41] This suggestion was made by Dr. V. K. La Mer.

liters of gas around the electrode. High values for log K_0 mean a better oxidizing (weaker reducing) agent or condition and vice versa, just as p_H indicates greater alkalinity or lower acidity.

Apparatus and Materials

The equipment consisted of a Leeds and Northrup type K potentiometer, a galvanometer of high resistance with a sensitivity of 424 megohms, a period of 2.8 seconds, and an external critical damping resistance of 2,000 ohms. The Weston cell was checked with others in the laboratory and found to be 1,0187 volts as certified to by the manufacturer. A Freas water bath constant to 0.01°C. was used. Three saturated calomel cells were employed and checked daily with one another to 0.1 millivolt for all results herein recorded.

The titrations were performed in a deep 400 cc pyrex beaker without lip fitted with a carefully cleaned rubber stopper, through which holes were bored to hold three electrodes, burette tip, salt bridge, and nitrogen inlet and exit tubes. The hydrogen electrode determinations were performed with the same apparatus, hydrogen only being exchanged for the nitrogen and platinized electrodes for the gold. Tank hydrogen was passed through mercuric chloride, acid permanganate, and twice through alkaline pyrogallate solutions, followed by cotton wool before passing into the Fisher bottles containing some of the buffer solutions for saturating with water vapor. Barometric and vapor pressure corrections were made in all cases. The nitrogen was passed through fresh pyrogallate and then through one foot of tightly rolled copper gauze heated to 700-800°C.

The salt bridge consisted of a glass tube of 4 mm bore fitted with a glass stopper[42] ground sufficiently tight to prevent diffusion of the quinone substances and KCl at the junction. (See figure IV). Good conductivity was obtained through the joint. The salt bridge and calomel cells dipped into a beaker containing saturated KCl.

The inlet and exit tubes for the nitrogen carried ground glass stop cocks so that there could be no diffusion of oxygen back to affect the determination of the end point. This is extremely important where very weak titanium solution is used.

[42] Suggested by Mr. L. Hammett.

The electrodes were either pure gold, gold-plated platinum, or platinum. In making the gold-plated electrodes a current density of 1/6 milliampere was used and the process continued from 4 to 7 hours. In the early stages of the work it was found that electrodes which gave sharp and stable potentials at first did not always continue to do so and new electrodes did not check them. Since Clark also speaks of having to retire electrodes from duty it may be well to mention the causes for this as found here. First, a very minute and gradual leakage of mercury through the seal was found to take place either with pyrex glass or soft glass electrodes that were heated and cooled often. This was too minute to be perceptible, but was proven by drawing it through under the influence

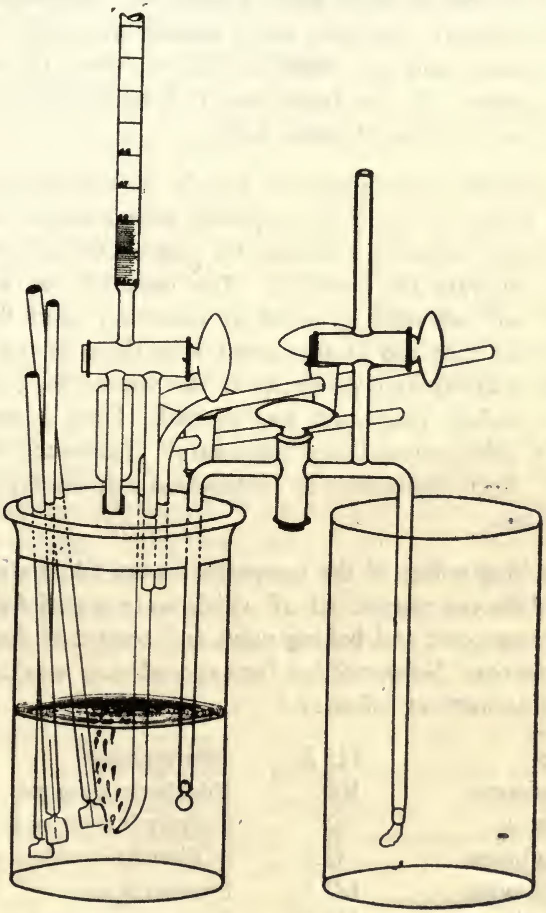

Figure IV

of a strong current. Secondly, electrodes left standing in distilled water acquired a film that was not removed by boiling or chromic acid. These electrodes gave identical potentials checking each other perfectly on any one solution at any one time, but those potentials were not stable. It is therefore evident that checking of electrodes is no true criterion of their good condition. Additional criteria must be met, namely, that they reach equilibrium with the solution in 2 to 3 minutes and are stable to .02 mv. when the solution is thoroughly shaken. It was found best to keep the electrodes in an acid solution or in weak chromic acid.

The quinones were prepared by the oxidation of the corresponding amine or hydroxy compound with acidified dichromate in an ice-cooled solution, followed by steam distillation wherever possible to separate the product. The materials were then recrystallized and sublimed as often as necessary until the melting points were constant and in agreement with those in the literature. No difficulty was experienced except in the case of the chlorquinone where some dichlor compound was formed. Here 3 recrystallizations and 4 sublimations were necessary. Exposure to light is deleterious. Recrystallization or sublimation was always performed just before use.

The melting points of the compounds were taken with thermometers of different ranges, all of which were tested for accuracy of the freezing point and boiling point and compared for intervening temperatures. No correction for exposed stem was made. The melting points were as follows:

quinone	115.7	chlorquinone	57.
hydroquinone	169.	chlorhydroquinone	102.
toluquinone	67.	bromhydroquinone	110.
thymoquinone	45.6	m dimethoxyquinone	248-249
p xyloquiuone	123.5	bromquinone	55.
napthaquinone	124.5	m dichlorquinone	120.*

The acidity of the titanous chloride solution used in making up the titrating solutions was determined by titration with NaOH in the presence of M/20 citric acid to prevent precipitation of titanic hydroxide. Sufficient M/5 HCl and distilled water were then added to make a solution of *exactly* the same acidity as that of the buffer solution in the beaker, in order that there should be no change of acidity due to the addition of the titrating agent itself. The solutions were kept under hydrogen in the manner described by Thornton.[43]. The strength of this solution varied from .005N to .030 N, though solutions stronger than .007 N would not keep indefinitely without precipitation at the concentration of hydrogen ion used. The dichromate solution contained 0.5 gm $K_2Cr_2O_7$ per liter of the same HCl buffer as was used to dissolve the hydroquinones.

Procedure

The apparatus being assembled the beaker was filled with 50, 75 or 100 ccs of buffer solution and the nitrogen bubbled through for an hour and a half or more to free the system from oxygen. The quinone compound, freshly resublimed, was then introduced through the burette tip hole in quantity sufficient to make about a .001 to .003 molar solution, the burette replaced and all sealed over with paraffin. The flow of nitrogen was stopped after another half hour and the titration begun. The apparatus was so arranged that the solution in the beaker could be vigorously shaken by hand after each addition. Equilibrium was thus reached in 2 to 3 minutes. Readings were taken every 2 minutes for 6 to 10 minutes or until it was certain that a constant and reproducible potential was obtained that was unaffected by moderate anodic or cathodic polarization, the solution being thoroughly shaken between each reading. The results were recorded to the nearest .05 mv. within which limit the separate electrodes checked. Table XV is given to illustrate the way in which the record was taken, to give some idea of the time required and to show how closely the electrodes checked. The end point was determined by plotting $\Delta\pi/\Delta\nu$ against the volume. Considerable time was necessary to reach equilibrium at the extreme end of the titration. In fact, a perfect equilibrium was probably not obtained but by adding the titrating agent toward the end in portions of 0.1 or 0.2 cc no difficulty was experienced in determining the sudden increase in $\Delta\pi/\Delta\nu$ and therefore determining the end point to within at least .05 to .1 cc, which is sufficiently accurate for the purpose.

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[43] Thornton, Jour. Am. Chem. Soc. *43*, 91 (1921).

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TABLE XV

Titration of 21 mg. hydroquinone with $K_2Cr_2O_7$

Time	cc $K_2Cr_2O_7$	E_1 gold	E_2 platinum	E_3 gold	$\Delta\pi/\Delta V$
1.10	2.00	.3811	.3811	.3811	
1.12		$.3811_5$	$.3811_5$	$.3811_5$	
1.14		.3811	.3811	.3811	
1.16	3.00	$.3872_5$	.3873	.3873	$.0062_5$
1.18		$.3873_5$	$.3873_5$	$.3873_5$	
1.20		$.3873_5$	$.3873_5$	$.3873_5$	
1.22	4.00	$.3919_5$	$.3919_5$	$.3919_5$	.0046
1.24		$.3919_5$	$.3919_5$	$.3919_5$	
1.26		$.3919_5$	$.3919_5$	$.3919_5$	
1.28	5.00	.3956	.3957	$.3957_5$	.0038
1.30		$.3957_5$	$.3957_5$	$.3957_5$	
1.32		$.3957_5$	$.3957_5$	$.3957_5$	
1.34	6.00	$.3989_5$	$.3990_5$	$.3990_5$	.0033
1.36		$.3990_5$	$.3990_5$	$.3990_5$	
1.38		$.3990_5$	$.3990_5$	$.3990_5$	
1.40	7.00	.4020	$.4020_5$	$.4020_5$	.0030
1.42		.4020	$.4020_5$	$.4020_5$	
1.44		.4020	.4020	.4020	
1.46	8.00	.4047	$.4047_5$	$.4047_5$	$.0027_5$
1.48		.4047	$.4047_5$	$.4047_5$	
1.50		.4047	$.4047_5$	$.4047_5$	
1.52	9.00	.4074	$.4075_5$	$.4075_5$	$.0028_5$
1.54		$.4075_5$	.4076	.4076	
1.56		$.4075_5$	.4076	.4076	
1.58	10.00	$.4103_5$	.4104	.4104	$.0028_5$
2.00		.4104	$.4104_5$	$.4104_5$	
2.02		.4104	$.4104_5$	$.4104_5$	
2.04	11.00	.4032	.4033	.4033	$.0028_5$
2.06		$.4033_5$	$.4033_2$	$.4033_2$	
2.08		.4033	$.4033_5$	$.4033._5$	
2.10		$.4033_2$	$.4033_2$	$.4033_2$	
2.12	12.00	.4161	.4163	.4163	.0030
2.14		.4163	$.4163_5$	$.4163_5$	
2.16		.4163	.4163	.4163	
2.18	13.00	.4195	$.4195_5$	.4195	.0033
2.20		$.4195_5$	.4196	.4196	
2.22		$.4195_5$	.4196	.4196	

Time	cc $K_2Cr_2O_7$	E_1 gold	E_2 platinum	E_3 gold	$\Delta\pi/\Delta V$
2.24	14.00	.4232	$.4232_7$	$.4232_7$	.0037
2.26		$.4232_7$	.4233	.4233	
2.28		.4233	.4233	.4233	
2.30	15.03	.4278	.4279	.4279	.0046
2.32		$.4279_3$	$.4279_5$	$.4279_5$	
2.34		.4279	.4279	.4279	
2.36	16.00	$.4333_5$	$.4334_5$	$.4334_5$	$.0065_5$
2.38		$.4334_3$	.4335	.4335	
2.40		$.4334_3$	$.4334_5$	$.4334_5$	
2.42	17.00	.4419	.4421	.4421	$.0086_5$
2.44		.4421	.4421	.4421	
2.46		.4421	.4421	.4421	
2.48	17.50	.4499	.4500	$.4501_5$	.0157
2.50		$.4499_5$	$.4499_5$	$.4499_5$	
2.52		$.4499_5$	$.4499_5$	$.4499_5$	
2.54	17.80	.4569	.4569	.4570	.0167
2.56		.4562	.4562	.4562	
2.58		.4560	.4560	.4560	
3.00		.4556	.4556	.4556	
3.02		.4555	.4555	.4555	
3.04		$.4554_5$	$.4554_5$	.4554	
3.06		.4552	.4552	.4552	
3.08		$.4549_5$	$.4549_5$	$.4549_5$	
3.10	18.00	.468			.0500
3.12		.466			
3.15		.465			
3.20		.465			
3.22	18.10	.470			.1000
3.24		.4765			
3.26		.476			
3.28		.476			
3.30		.476			
3.32	18.20	.496			.5300
		.520			
		.525			
		.529			
		.520			
		.533			
		.531			
		.529			

Time	cc $K_2Cr_2O_7$	E_1 gold	E_2 platinum	E_3 gold	$\Delta\pi/\Delta V$
4.20	18.30	.550			.3300
		.565			
		.563			
5.00		.562			
5.00	18.40	.577			.2000
		.579			
		.580			
		.581			
		.581			
		.582			
5.40		.582			
5.40	18.50	.589			.0800
		.590			
		.591			
		.590			
6.20		.590			

SUMMARY

1. A beginning has been made on the study of the relation of structure of organic compounds to their oxidation-reduction potentials and the corresponding free energy changes, by investigating the effect due to the brom, chlor, di chlor, methyl, di methyl, methyl isopropyl, methoxy and phenylene groups when substituted in the quinone nucleus.

2. The data are discussed in the light of the positive and negative rule of Michael, and compared with similar data on the free energy of ionization.

3. The validity of the electrometric titration method of measuring the oxidation-reduction potentials of these organic compounds has been discussed and established experimentally by meeting the criteria of (a) constancy and reproducibility of the potentials under widely varying concentrations, and following anodic and cathodic polarizations; (b) reproducibility using different electrode materials; (c) agreement of the E.M.F. with the values obtained by the method of mixtures; and (d) by approaching the equilibrium from both sides.

4. The errors due to variation in contact potential, activities of components, quinhydrone formation, and the like, have been eliminated or rendered negligible, and apparatus and technique developed with the result that a precision of ±0.2 millivolts has been attained. Purity of compounds has been shown to be important in obtaining precise results.

VITA

Lillian Eloise Baker was born in 1890 in Wheaton, Illinois. She received the degree of Bachelor of Arts from Wellesley College in 1914 and the degree of Master of Arts from Columbia Univrsity in 1919. From 1914 to 1918 she was instructor in Pratt Institute, Brooklyn, New York, and from 1918 to February, 1921, instructor in Wellesley College. She was enrolled as a student at Columbia University during the summers of 1918-1920 and continuously from February, 1921, to August, 1922. During the period of this investigation she held a University Fellowship and is at present Research Assistant at the Rockefeller Institute for Medical Research.

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